

Supplemental Material:

Reabsorption of Soft X-ray Emission at High X-ray Free-Electron Laser Fluences

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S1 X-ray spot size and fluence determination

For accurate determination of the x-ray spot size on the sample we used a thin YAG crystal in the sample plane and a long working distance microscope system (Infinity Photo-Optical Company, Model K2/SC) to record images of the fluorescence induced by the heavily attenuated XFEL

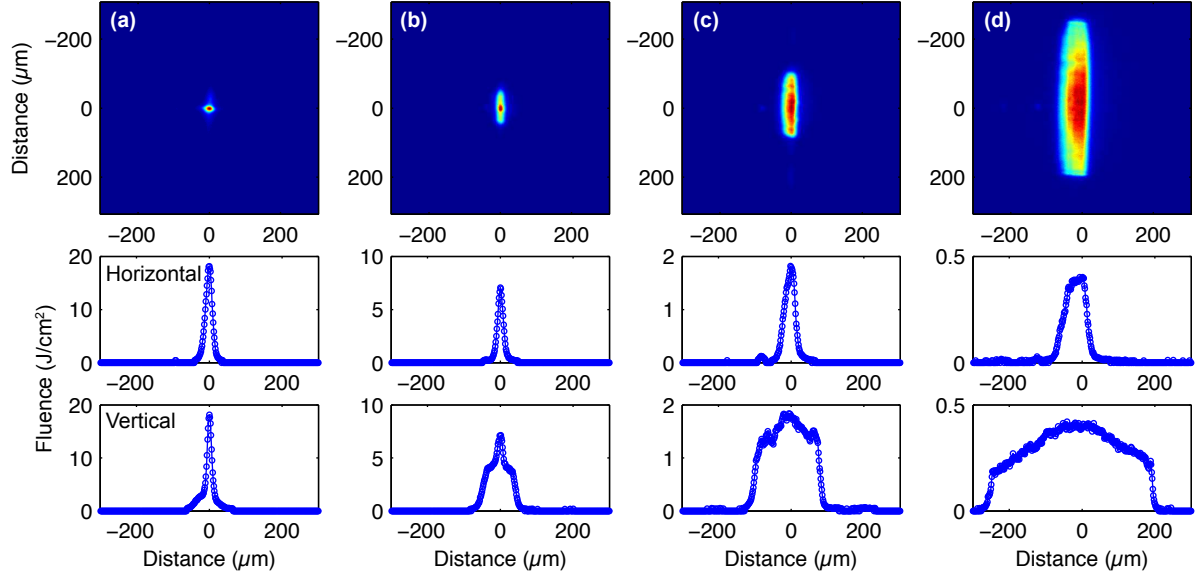


Figure S1: The four different spot sizes that were used during the experiment to reach a large fluence range. The spot size was changed by bending and unbending the focusing optics of the beam line. Additional fluence range was covered with a gas attenuator. The fluence is given for a pulse energy of 1 mJ.

beam in the crystal. The microscope system had a resolution of $3 \mu\text{m}$ and one pixel on the CCD camera corresponded to a size of $1.5 \times 1.5 \mu\text{m}^2$. In Figure S1 we show the microscope images after background subtraction together with cuts along the horizontal and vertical dimension through the intensity maximum.

A first calibration of the fluence was performed directly from the intensity profile of each spot and the fluence in the spot maximum was used. To increase the accuracy in the relative fluence calibration between the different spot sizes, spectra measured at the same fluence but with different spot sizes were compared and the fluence calibration was slightly adjusted to give the same spectral shape for the same incident fluence. These adjustments accounted for inhomogeneities in the x-ray spot profile.

For each spot size we performed a scan of the gas attenuator without adjusting the relative alignment of x-ray beam, liquid micro jet as well as x-ray emission spectrometer to not change the total signal strength. The time for individual scans was short compared to the timescale of drifts in the experimental alignment. Scans with sudden changes in the alignment (e.g. liquid jet movements) were excluded from the analysis. However, the exact same experimental alignment could not be guaranteed for attenuator scans for different spot sizes. Therefore the integrated emission intensity was normalized for each attenuator scan to give the same number of emitted photons for the same number of incident photons hitting the jet. The normalization factors finally differed by about 30%.

S2 Explicit derivation of the number of observed photons

We describe the number of photons N_{obs} , which are traveling towards the spectrometer (in y -direction) and hence get observed in our experiment. The number changes with distance y in the excited volume due to spontaneous emission and reabsorption, while we neglect evolutions in other directions. We therefore describe N_{obs} by the differential equation

$$\frac{dN_{\text{obs}}}{dy} = \frac{dN_{\text{emit}}}{dy} - \frac{dN_{\text{reabs}}}{dy} \quad (\text{S1})$$

with $N_{\text{obs}}(y = 0) = 0$ at the far end of the excitation volume with respect to the spectrometer position.

N_{emit} gives the number of spontaneously emitted photons into the spectrometer direction and N_{reabs} gives the number of reabsorbed photons.

For N_{emit} we write:

$$N_{\text{emit}}(y, E, N_{\text{in}}) = A N_{\text{in}} \frac{y}{Y} \frac{\sigma_{\text{emit}}(E)}{\Sigma}. \quad (\text{S2})$$

A is a scaling parameter that depends on the quality of the alignment, i.e. the overlap between the x-ray beam and the liquid micro jet. Additionally, it includes the fluorescence yield as well as the angular acceptance and detection efficiency of the spectrometer. It will be the only free parameter in the model and will be determined from the fit to the experimental data. See also section S4.

N_{in} is the number of incident photons. For x-ray spot sizes with a horizontal dimension bigger than the jet diameter N_{in} is scaled accordingly. We assume, that all photons hitting the liquid jet get absorbed within the irradiated volume, exciting oxygen 1s core-level electrons.

Assuming a constant core-excitation density across the excited volume, the number of photons emitted towards the spectrometer N_{emit} increases linearly with distance y in the excited volume starting from $N_{\text{emit}} = 0$ at the far end of the excitation volume ($y = 0$) with respect to the spectrometer position up to its maximum at $y = Y$. Y is determined by the dimension of the excited volume along the spectrometer direction.

σ_{emit} is the emission cross-section that depends on the considered emission energy channel E , while Σ is the total emission cross-section over the complete XE spectrum: $\Sigma = \int \sigma_{\text{emit}}(E) dE$.

Following the Lambert-Beer law, the number of photons traveling towards the spectrometer that get reabsorbed on an infinitesimally short distance dy in the valence-excited volume is given by

$$dN_{\text{reabs}}(y, E, N_{\text{in}}) = N_{\text{obs}}(y) \sigma_{\text{reabs}}(E) \rho_{\text{vh}}(N_{\text{in}}) dy. \quad (\text{S3})$$

The reabsorption cross-section σ_{reabs} is determined by the dipole transition matrix element between the O 1s core level and the valence level. It is therefore identical to the corresponding emission cross-section, that represents the inverted transition between the same levels: $\sigma_{\text{reabs}} =$

$\sigma_{\text{emit}} = \sigma$. $\rho_{\text{vh}}(N_{\text{in}})$ represents the valence hole density and depends on the number of incident photons (see section S3). We assume that the valence holes are distributed evenly over the available valence levels. Thus, their spectrum is identical to the valence electron spectrum (x-ray emission spectrum) and the energy dependence of N_{reabs} is given through the reabsorption cross-section $\sigma(E)$.

The differential equation (S1) for the number of observed photons thus reads

$$\frac{dN_{\text{obs}}(y, E, N_{\text{in}})}{dy} = A N_{\text{in}} \frac{1}{Y} \frac{\sigma(E)}{\Sigma} - N_{\text{obs}}(y) \sigma(E) \rho_{\text{vh}}(N_{\text{in}}). \quad (\text{S4})$$

To obtain the number of photons that get observed in the spectrometer as a function of incident photons N_{in} and emission energy E , we evaluate the solution of (S4) at $y = Y$:

$$N_{\text{obs}}(E, N_{\text{in}}) = \frac{A N_{\text{in}}}{Y \Sigma \rho_{\text{vh}}(N_{\text{in}})} (1 - \exp(-\sigma(E) \rho_{\text{vh}}(N_{\text{in}}) Y)) \quad (\text{S5})$$

This expression (S5) is fitted to the experimental data.

S3 The valence hole density

For the description of the valence hole density ρ_{vh} as a function of incident photon number N_{in} we consider the simplified density of occupied and unoccupied states in liquid water as depicted in Figure S2(a). The density of states is approximated as two boxes. The occupied and unoccupied states each have an energy width of E_{W} and are separated by the HOMO-LUMO separation energy E_{BG} (band gap). For the occupied states we consider the six outer valence electrons of the water molecule, which defines together with E_{W} the density of occupied states. For the unoccupied states we assume the same density of states.

We now consider the energy E_{vh} needed to create a valence hole in a molecule as a function of the number of already existing valence holes ρ_i in this molecule. (Using the number density of molecules, all these quantities can be easily converted from numbers to densities.) If there is already one valence hole that occupies exactly one state in the density of states, the creation of the next valence excitation needs more energy. This energy increases stepwise with each additional valence hole in an individual molecule. However, since we consider the average over the ensemble of molecules in the excited volume, the average needed energy E_{vh} increases linearly from the energy gap E_{BG} up to the full depletion of the valence band at $E_{\text{BG}} + 2 E_{\text{W}}$ as illustrated in Figure S2(b). E_{vh} can therefore be expressed as

$$E_{\text{vh}}(\rho_i) = E_{\text{BG}} + \frac{2 E_{\text{W}}}{6 \frac{\text{valence holes}}{\text{molecule}}} \rho_i \quad \text{for } \rho_i < 6, \quad \infty \text{ else.} \quad (\text{S6})$$

To obtain the total energy E_{tot} needed to create a valence hole density of ρ_{vh} , we integrate E_{vh}

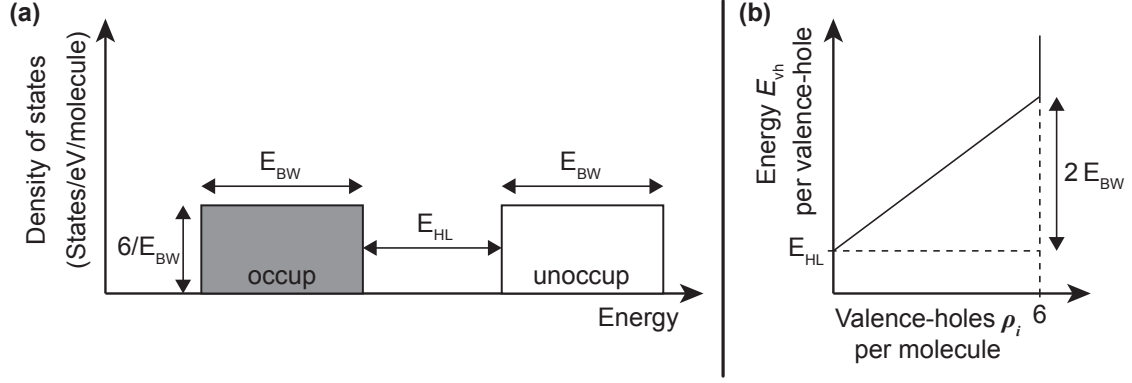


Figure S2: The simplified scheme for the density of states in water, as it is used to model the valence hole density after strong excitation.

up to ρ_{vh} :

$$E_{\text{tot}}(\rho_{\text{vh}}) = \int_0^{\rho_{\text{vh}}} E_{\text{vh}}(\rho_i) d\rho_i = E_{\text{BG}} \rho_{\text{vh}} + \frac{1}{6} E_{\text{W}} \rho_{\text{vh}}^2. \quad (\text{S7})$$

Solving equation (S7) for ρ_{vh} we obtain an expression for the number of valence holes in a molecule as a function of the total energy deposited in the molecule:

$$\rho_{\text{vh}} = -\frac{3E_{\text{BG}}}{E_{\text{W}}} \pm \sqrt{\left(\frac{3E_{\text{BG}}}{E_{\text{W}}}\right)^2 + \frac{6E_{\text{tot}}}{E_{\text{W}}}}. \quad (\text{S8})$$

In equation (S8) only the '+'-term gives a physical solution. The total energy deposited in a molecule is given by $E_{\text{tot}} = \frac{N_{\text{in}} \times 550 \text{ eV}}{n_{\text{mol}}}$, where n_{mol} is the number of molecules in the excitation volume. We therefore find $\rho_{\text{vh}} \propto \sqrt{N_{\text{in}}}$. At this point (S8) gives the number of valence holes per molecule. To obtain the valence hole density we multiply by n_{mol} .

S4 Parameters

The parameters used for the fit to the experimental data are given in Table S1.

The interaction length Y is given by the dimension of the excited volume along the detection direction and was determined by geometrical considerations (see Figure S3).

The excited volume forms a thin curved sheet on the liquid jet surface (Figure 1 of the main text) and was determined by the vertical x-ray spot size, the jet diameter (since the horizontal x-ray spot size was always bigger or identical than the jet diameter) and the absorption length of 550 eV x-ray photons in liquid water (Ref. [20] from the main text).

The value for Σ was approximated from the tabulated x-ray absorption cross-section (Ref. [20] from the main text) assuming an approximately two times bigger cross-section for the emission process due to the more localized character of the occupied valence levels as compared to the unoccupied valence levels. The energy dependence of $\sigma(E)$ is taken from the measured undistorted

XE spectrum and its magnitude is defined by $\Sigma = \int \sigma(E)dE$.

The value for E_W was approximated from the measured x-ray emission spectrum.

The exact value for the HOMO-LUMO separation energy in liquid water E_{BG} (band gap) is debated. See e.g. [1]. We determined the value from RIXS spectra excited in the onset of the x-ray absorption resonance by taking E_{BG} as the difference between the excitation energy and the onset of the emission from the HOMO. The obtained value lies within the values discussed in [1].

The value for A was determined from the fit to the experimental data. It agrees well with the expected value recalling that A accounts for the fluorescence yield (5×10^{-3} at the oxygen K-edge, Ref. [24] of the main text) as well as for the angular acceptance (10^{-5} , Refs. [12, 14] from the main text) and detection efficiency (10^{-2} , Refs. [12, 14] from the main text) of the spectrometer.

Parameter	Value
Y	$8 \mu\text{m}$
Σ	$1 \times 10^{-22} \text{ m}^2$
E_W	7 eV
E_{BG}	7.3 eV
ρ_{mol}	$3.3 \times 10^{28} \text{ m}^{-3}$
A	$(0.41 \pm 0.01) \times 10^{-10}$

Table S1: Parameters used for the fit to the experimental data.

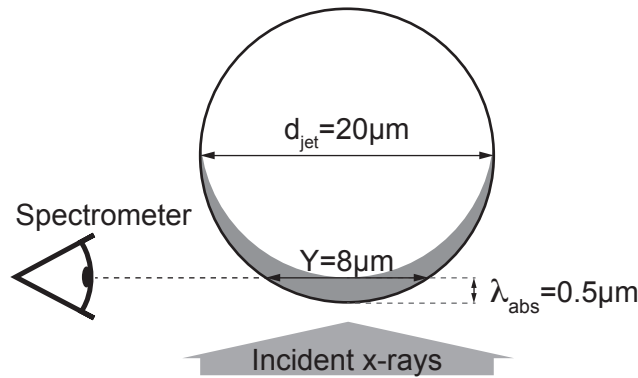


Figure S3: Schematic cut through the liquid jet perpendicular to the direction of the liquid flow to illustrate the interaction length Y . Drawing is not to scale.

References

- [1] A. Bernas, C. Ferradini, and J.-P. Jay-Gerin, “On apparent contradictions in some photo-physical properties of liquid water,” *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 117, pp. 171–173, Sept. 1998.